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Reactivity of PtII "Pincer" Complexes with Carbon Monoxide

Margaret L. Scheuermann
Scripps College

Reactivity of Pt^{II} "Pincer" Complexes with Carbon Monoxide

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by

Margaret L. Scheuermann

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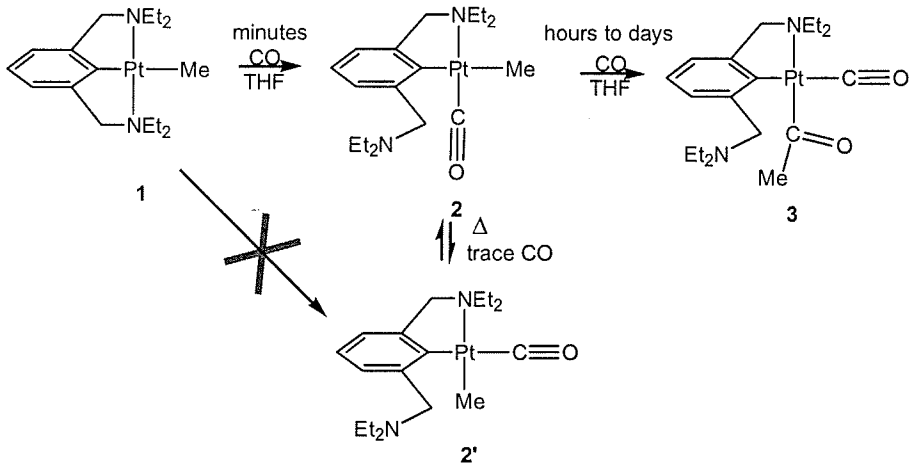
Abstract

Upon addition of carbon monoxide (CO) to a solution of (κ-*N,C,N*-2,6-bis(diethylaminomethyl)-phenyl)methyl platinum(II), [NCN]PtMe, **(1)**, a ligand arm is displaced to form [SP-4-2] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II), N[CN]Pt(CO)(Me), **(2)**. Addition of CO to a THF solution of **2** results in the formation of [SP-4-3] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)acylcarbonyl platinum(II), N[CN]Pt(Ac)(CO), **(3)**. In THF, **2** partially isomerizes in the presence of CO to form [SP-4-4] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II), N[CN]Pt(Me)(CO), **(2')**, in equilibrium with **2** (K = ca. 2 at 100 °C). In the absence of CO, only trace isomerization was observed. Thermolysis of **3** results in the formation of a mixture of **2** and **2'**, while a reaction of **3** with trimethylamine N-oxide results exclusively in the formation of **2**. Both three and five-coordinate intermediates have been shown to be accessible, leading to two proposed mechanisms for the thermolysis of **3** and the microscopic reverse of this reaction.



Introduction

Transition Metal Carbonyl Complexes

Organometallic chemistry is the study of compounds containing metal-carbon bonds. One important class of organometallic compounds, carbonyl complexes, is comprised of species containing a carbon monoxide (CO) ligand. A feature characteristic of many carbonyl complexes is the ability of the metal to engage in backbonding to the carbonyl.[1] As is the case in a typical metal-ligand σ bond, the CO ligand donates electron density to the metal center. In the backbond, however, a full metal *d*-orbital donates electron density to the π^* orbital on the ligand (Figure 1). This bonding can also be described using the resonance structures shown in Figure 2.

Figure 1. Molecular orbital overlap involved in backbonding (on left) and direction of electron flow (on right)

Figure 2. Metal backbonding to a carbonyl

The molecular orbital picture of backbonding is similar to that offered by the Dewar-Chatt-Duncanson model for alkene-metal bonds.[2,3] In an M-CO bond the contribution of backbonding to the final structure varies with the metal involved, oxidation state, and other ligands present.

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
[2] Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.
[3] Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1952**, 2939.

This molecular orbital description of backbonding is supported by physical evidence. Typical C-O bond lengths in carbonyl complexes are 1.12 to 1.18 Å, somewhat longer than the C-O bond length of free CO (1.128 Å).[4] The longer bond length reflects the decrease in C-O bond order resulting from the donation of electrons into an antibonding orbital for the C-O bond. Similarly, the IR stretching frequencies of bound carbonyls are typically lower (2125 to 1850 cm^{-1}) than that of free CO (2143 cm^{-1}), also consistent with a weaker, longer bond.[4] Metal carbonyl complexes are also frequently characterized by ^{13}C NMR spectroscopy. ^{13}C NMR chemical shifts for metal carbonyls are typically in the range of 190 to 200 ppm but can deviate significantly from this range depending on surrounding ligands.[5]

Industrial Applications of Transition Metal Carbonyl Complexes

Reactions of CO at transition metal centers have numerous current and potential applications in industrial processes. In the Monsanto acetic acid process, methanol and CO are combined over a rhodium catalyst in the presence of iodide to generate acetic acid.[6] The reaction proceeds under modest temperature and pressure conditions, 180 °C and 30-40 atm. When this process was developed, it was sufficiently superior to any existing method that its introduction rendered all other processes obsolete.[1] Rhodium and iodide can be introduced from various sources and in the presence of CO and methanol will combine to generate an anionic complex of the form $[Rh(CO)_2I_2]^-$ and methyl iodide. Subsequent mechanistic steps are understood to consist of the oxidative addition of methyl iodide followed by a formal carbonyl insertion and reductive

[4] See reference 1 page 114.
[5] Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975; 240-243.
[6] Roth, J. F.; Craddock, J. H.; Hershman, A.; Paulik, F. E. *Chem. Tech.* **1971**, *1*, 600.

elimination of acetyl iodide. The conversion of acetyl iodide to acetic acid and iodic acid occurs in the presence of water. This catalytic cycle is summarized in Figure 3.

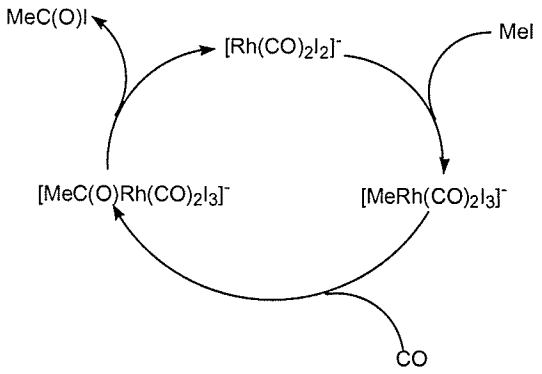

Figure 3. Monsanto acetic acid process catalytic cycle

Another catalytic cycle involving carbon monoxide which has been studied for nearly a century is the Fischer-Tropsch process. This reaction converts a mixture of CO and hydrogen gas known as synthesis, or "syn" gas into a mixture of products including long chain alkanes that serve as a useful liquid fuel.[7] Germany during WWII and South Africa during the *apartheid* era used coal to generate the synthesis gas needed for the Fischer-Tropsch process.[8] Synthesis gas can also be generated from natural gas (primarily methane) and there are plants in Malaysia and New Zealand that presently use this technology for liquid fuel production. Though the mechanism of this reaction is not well understood, there are several possibilities that have received significant consideration. Fischer and Tropsch originally proposed a mechanism involving carbene polymerization.[9] This mechanism has been updated to suggest that the process begins with the formation of a methyl group on the catalyst surface.[10] The methyl group then repeatedly inserts CH_2 fragments. A study using ^{13}C labeled CO supports this

[7] Rofer-DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447.
[8] Olah, G. A.; Goeppert, A.; Surya Prakash, G. K. *Beyond Oil and Gas: The Methanol Economy*; WILEY-VCH Verlag GmbH & Co.: Weinheim, 2006.
[9] Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97.
[10] Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

mechanism.[11] A less probable mechanism suggests that the reaction proceeds as a surface reaction between hydroxymethylene groups.[12] Yet another proposal is that the reaction proceeds as a formal carbonyl insertion (see below).[13]

There has been much study of the copolymerization of olefins and CO, particularly using palladium catalysts.[14] The active catalysts are thought to be square-planar cationic d^8 complexes. The propagation steps involve an alternating series of formal CO insertions into Pd-alkyl bonds and insertions of the olefin into the Pd-acyl bond.[15,16] While the former step is well precedented and will be discussed further, the latter step is much more unusual but is favorable in the case of the palladium catalysts studied.

Another important process involving a reaction of CO at a metal center is hydroformylation, also referred to as the oxo reaction. This reaction catalytically converts syn gas and α–olefins into linear and branched aldehydes. The mechanism of this reaction is not thoroughly understood for all catalysts and it is thought to vary from system to system.[17,18]

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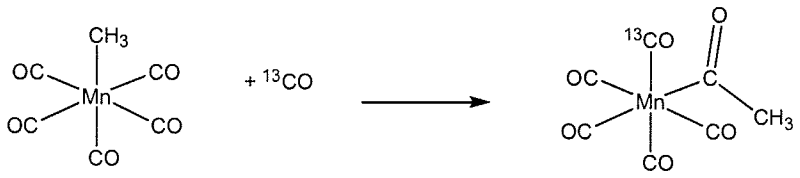
[11] Biloven, P.; Helle, H. N.; Sachtler, W. M. H. J. *Catal.* **1979**, *58*, 95.
[12] Kummer, J. F.; Emmett, P. H. *J. Am. Chem. Soc.* **1953**, *75*, 5177.
[13] Pichler, H.; Schultz, H. *Chem. Eng. Tech.* **1970**, *12*, 1160.
[14] Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.
[15] van Leeuwen, P. W. M. N.; Roobeek, C. F.; van der Heijden, H. J. *J. Am. Chem. Soc.* **1994**, *116*, 12117.
[16] Markies, B. A.; Kruis, D.; Rietveld, M. H. P.; Verkerk, K. A. N.; Boersma, J.; Kooijman, H.; Lakin, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1995**, *117*, 5263.
[17] *Rhodium catalyzed hydroformylation.* van Leeuween, P. W. M. N.; Claver, C. Eds. Kluwer Academic Publishers: Dordrecht, 2002.
[18] Cornils, B. Hydroformylation Oxo Synthesis, Roelen Reaction. In *New Syntheses with Carbon Monoxide.* J. Falbe, Ed.; Springer Verlag: Berlin, 1980; 1-225.

Mechanism of Formal Carbonyl Insertion

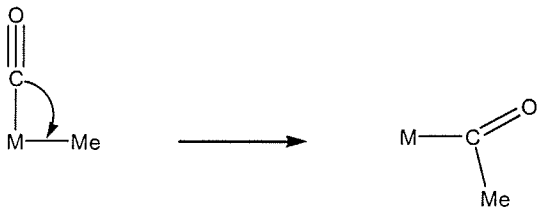
A fundamental transformation discussed in the context of several of the previous reactions is formal carbonyl insertion into a metal-carbon bond. A mechanism for this reaction was first elucidated by Noack *et al.* in an elegant labeling study monitored by IR spectroscopy.[19] The results of this study were later confirmed by ^{13}C NMR spectroscopy.[20] Noack and coworkers initially exposed $CH_3Mn(CO)_5$ to an atmosphere of ^{13}CO as shown in Scheme 1.



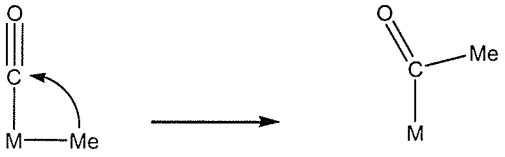
Scheme 1. Addition of labeled CO to $CH_3Mn(CO)_5$

This experiment offered three key mechanistic conclusions. Because no ^{13}CO was inserted it can be concluded that the inserted CO was initially bound to the metal rather than coming from added CO. The acyl group formed is located *cis* to the ^{13}CO indicating that the methyl group and the inserted CO were *cis* to one another initially. As no *trans* isomer formed, it can be concluded that no significant isomerization occurred. These results are consistent with *both* a carbonyl insertion (Scheme 2) and a methyl migration (Scheme 3).[21, 22]

[19] Noack, K.; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101.
[20] Flood, T. C.; Jensen, J. E.; Statler, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4410.
[21] Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209.
[22] The arrows in Scheme 2 and Scheme 3 are used to indicate the movement of atoms rather than electrons as is conventional in organic texts.



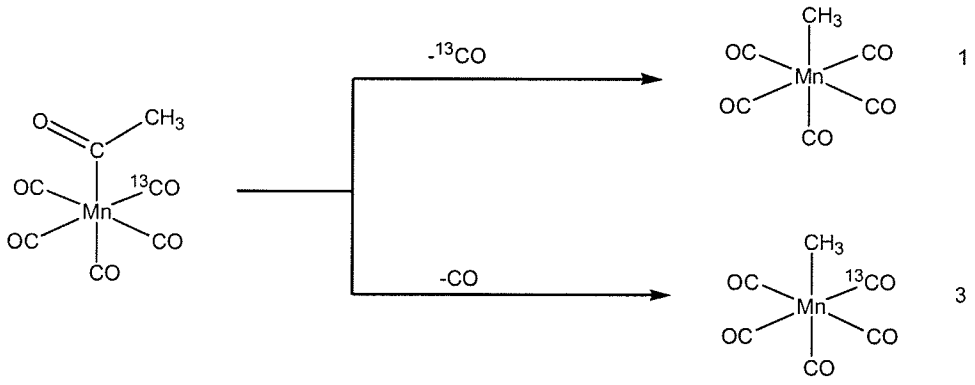
Scheme 2. Carbonyl Insertion



Scheme 3. Methyl Migration

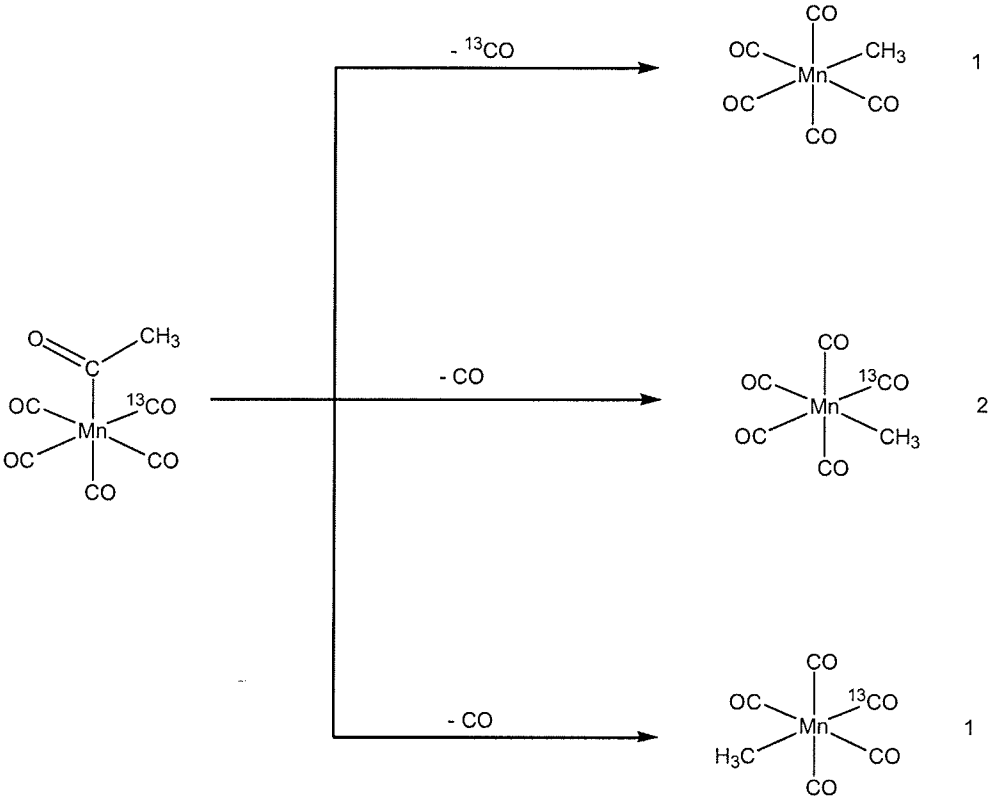
To distinguish between these two mechanisms, the researchers took advantage of the principle of microscopic reversibility, which states that the mechanism of a reaction in the forward and reverse directions will be identical.[23] As applied to the carbonylation reaction, the principle indicates that studying the decarbonylation mechanism could provide insight into the carbonylation mechanism. The complex studied was *cis*-$Mn(C(O)CH_3)(^{13}CO)(CO)_4$, which was then heated until decarbonylation occurred. In the reverse of the carbonyl insertion (Scheme 2) mechanism, the methyl group remained in the coordination site where the acyl was previously located and the carbonyl from the acyl group replaced another CO on the molecule in a site *cis* to the initial acyl site. This would yield $Mn(CH_3)(CO)_5$ and $Mn(CH_3)(^{13}CO)(CO)_4$ in a 1:3 ratio as shown in Scheme 4. Because of the requirement that the acyl group and the departing CO be *cis* to one another, there would be a one in four chance that the CO to leave would be the ^{13}CO.

[23] Tolman, R. C. *The Principles of Statistical Mechanics*. Oxford University Press: London, 1938.



Scheme 4. Decarbonylation mechanism if carbonyl insertion path were operative

If the methyl migration mechanism were operative, there would be three possible products as outlined in Scheme 5.



Scheme 5. Decarbonylation products if methyl migration path were operative

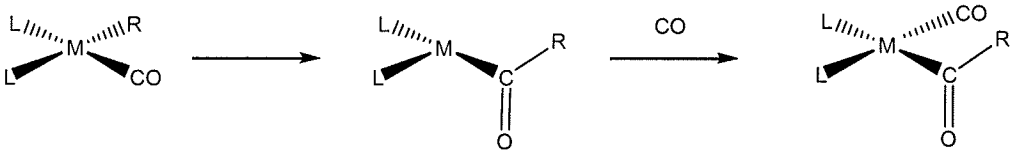
In this mechanism, it is the methyl group from the acyl that moves to the coordination site vacated by the departing CO, which again, must be *cis*. As a result the methyl group

can displace the ^{13}CO (25% chance), displace a CO that is *cis* to ^{13}CO (50% chance), or displace the CO that is *trans* to the ^{13}CO (25% chance).

The experimental results were consistent with the second mechanism, methyl migration (Scheme 5), for which the forward mechanism is shown in Scheme 3. Thus, although the term "insertion" is often used to describe the reaction involving a CO and alkyl ligand to form an alkyl carbonyl, the term is misleading, as the methyl migration mechanism is typically operative, especially in late metal systems.[24,25]

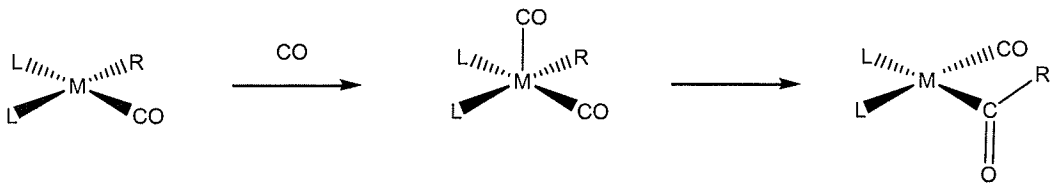
Migratory Insertion in Square Planar Complexes

Given their importance to a wide variety of catalytic cycles, platinum group square planar carbonyl complexes are particularly relevant systems for mechanistic study.[26] Reactions involving CO and square planar d^8 complexes involve an additional mechanistic question besides that of migration or insertion that was discussed more generally for metal complexes. While in a six coordinate complex the reaction must proceed dissociatively, in a square planar complex both associative and dissociative mechanisms are possible. The dissociative pathway for a formal insertion at a square planar complex involves a three coordinate intermediate as shown in Scheme 6, while an associative pathway involves a five coordinate intermediate as shown in Scheme 7.



Scheme 6. Dissociative pathway involving a three coordinate intermediate

[24] Anderson, G. K.; Cross, R. *J. Acc. Chem. Res.* **1984**, *17*, 67.
[25] van Leeuwen, P. W.N. M.; Roobeek, C. F.; van der Heijden, H. *J. Am. Chem. Soc.* **1994**, *116*, 12117.
[26] The platinum group generally refers to the second and third row metals in the iron, cobalt, and nickel triads.



Scheme 7. Associative pathway involving a five coordinate intermediate

Five coordinate intermediates of the form shown in Scheme 7 have been observed in low temperature NMR experiments.[27] The presence of such a five-coordinate intermediate allows for isomerization through a trigonal bipyramidal species.[1] There is significant literature support for both pathways and it is thought that the operative mechanism is dependant on the specific complex and reaction conditions.[21] In addition, there is evidence that solvent coordination may be involved in the mechanism in certain cases.[28]

[NCN]PtMe as a Potentially Interesting Substrate for Carbonyl Chemistry

The complex used for the studies discussed herein is of a form originally pioneered by Van Koten and coworkers, which has been given the name "pincer complex" for the meridional manner in which the ligand holds the metal.[29] In the past few decades, complexes of the form [NCN]PtX have found numerous sensing and catalytic applications.[30] Though this type of complex has been widely studied, the first simple alkyl derivative of such a complex was recently synthesized in the Williams group. Prepared from an [NCN]PtCl derivative, (κ-*N,C,N*-2,6-bis(diethylaminomethyl)-

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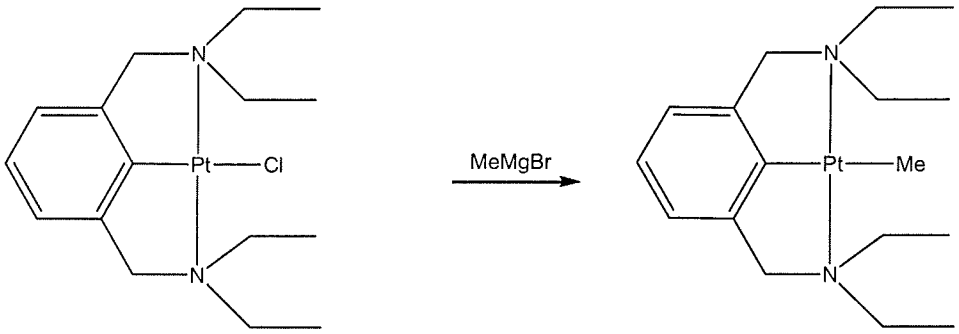
[27] Bryndza, H. E. *Organometallics*. **1985**, *4*, 1686.
[28] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028.
[29] Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609.
[30] Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

phenyl)methyl platinum(II), [NCN]PtMe (**1**), shown with its precursor in Scheme 8, has been previously used for studies of reductive elimination.[31]



(1)

Scheme 8. Synthesis of [NCN]PtMe (1)

Unlike many of the other complexes previously studied for CO reactivity, **1** contains a tridentate anionic ligand. The body of literature on systems containing polydentate ligands is much smaller, with most of the systems studied having neutral, bidentate ligands.[21,32] More fundamentally, this complex is relatively unusual because of the two mutually *trans* organic ligands. Computational studies have suggested that energy barriers to migration reactions are significantly lower when the group *trans* to the migrating group is a strong ligand, a result supported by experimental evidence.[33,34] Computational and experimental studies have found that migration reactions tend to have higher energy barriers at Pt than Pd, a result that has been rationalized by the greater Pt-C bond strengths.[35] Combining these ideas suggests that **1** may be an unusually CO reactive Pt complex.

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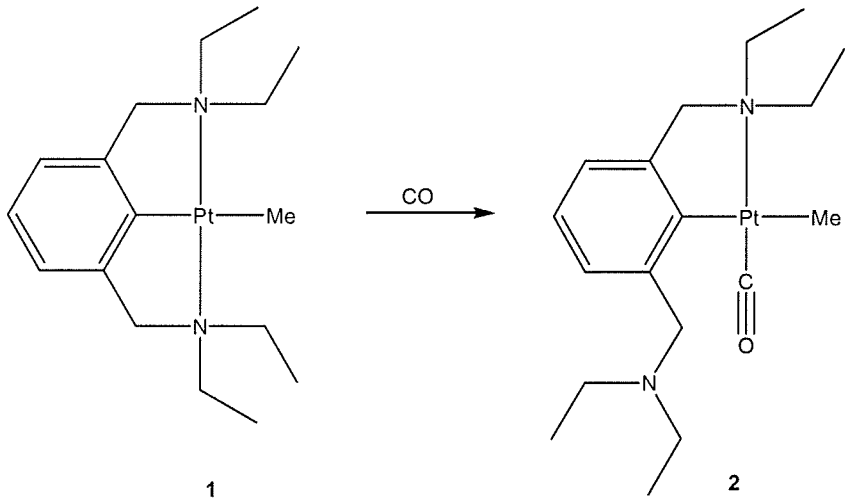
[31] Madison, B. L.; Thyme, S. B.; Keene, S.; Williams, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 9538.
[32] Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *Organometallics*, **1992**, *11*, 1598.
[33] Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *108*, 7230.
[34] Kubota, M.; McClesky, T. M.; Hayashi, R. K.; Webb, C. G. *J. Am. Chem. Soc.* **1987**, *109*, 7569.
[35] Kayaki, Y.; Tsukamoto, H.; Kaneko, M.; Shimizu, I.; Yamamoto, A.; Tachikawa, M.; Nakajima, T. *J. Organomet. Chem.* **2001**, *622*, 199.

Herein the reactivity of **1** with CO is explored and the products characterized. Experiments toward determining the mechanistic pathways involved in CO insertion at Pt^{II} complexes are discussed.

Results and Discussion

Reaction of [NCN]PtMe (1) with Carbon Monoxide

When **1** was dissolved in a wide variety of solvents (benzene-d_6, toluene-d_8, dichloromethane-d_2, THF-d_8, acetonitrile-d_3, and nitrobenzene-d_5) under an atmosphere of CO, formation of [*SP*-4-2] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II) (**2**) was observed within minutes (Scheme 9).[36] A variety of solvents were tested to determine the extent to which the reaction was dependant on solvent properties such as coordinating ability, polarity, or varying solubilities of CO.[37] This reaction exhibited essentially no solvent dependence.



Scheme 9. Conversion of [NCN]PtMe (1) to N[CN]Pt(CO)(Me) (2)

Infrared spectroscopy of **2** revealed a C-O stretching frequency of 2055 cm^{-1}, consistent with CO bound to Pt.[38] The ^1H and ^{13}C NMR spectra in benzene-d_6 were fully assigned with the assistance of HMQC and HMBC experiments (see Experimental section). These spectra indicate a reduction in symmetry from C_{2v} to C_s associated with the conversion of

[36] Novel CO complexes were named in accordance with guidelines presented in Huheey, J. E.; Keiter, E. A.; Keiter, R.L. *Inorganic Chemistry: Principles of Structure and Reactivity*. 4th ed. Harper Collins College Publishers: New York, 1993; A46-A77.
[37] Fogg, P. G. T.; Gerrard, W. *Solubilites of Gases in Liquids*. John Wiley & Sons: Chichester, 1991.
[38] Nakamoto, K. *Infared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley & Sons Inc.: New York, 1997.

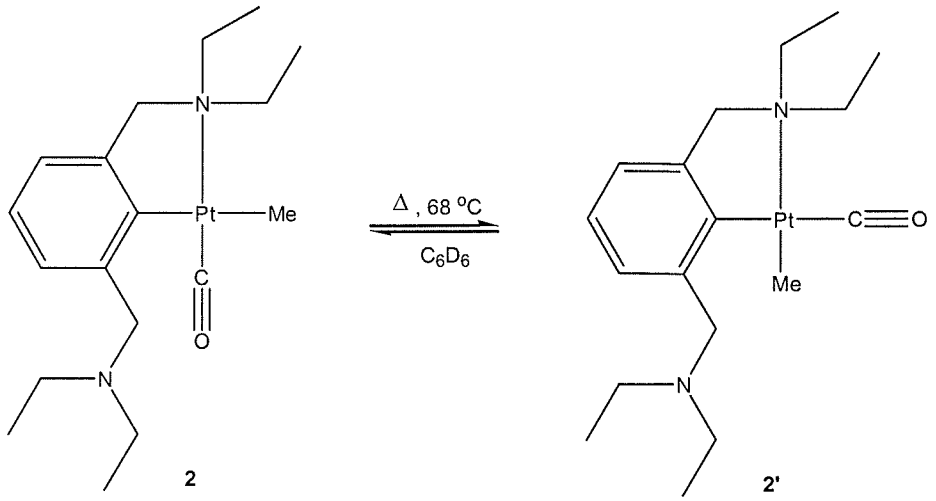
1 to **2**. The loss of diastereotopy in one of the amine arms on the ligand also suggests that one of the amine arms is no longer bound to Pt. The methyl group still appears to be *trans* to the aryl ring, as $^2J_{Pt\text{-}H}$ values for **1** and **2** are similar (48 Hz and 42 Hz, respectively). These relatively small Pt-H couplings are consistent with the methyl group being *trans* to a strong ligand such as an aryl group.[39]

While it would be desirable to isolate **2** for elemental analysis and crystal structure determination, this may prove difficult because, as of yet, **2** has not been isolated as a solid despite attempts to crystallize it from pentane, toluene, ether, benzene, *bis*-trimethylsilyl ether, dichloromethane, and tetrahydrofuran. Removing solvent *in vacuo* yields an oily substance.

Isomerization of N[CN]Pt(CO)(Me) (2)

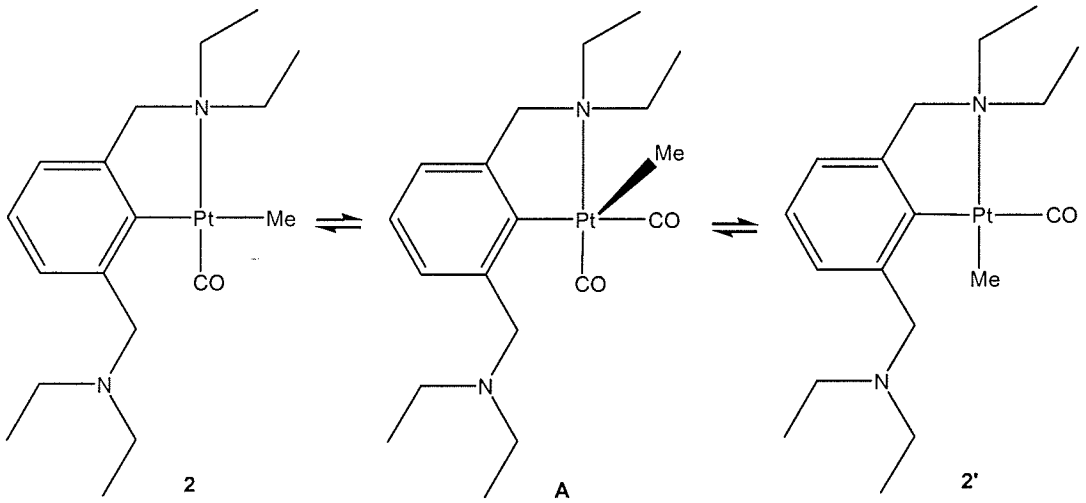
On heating **2** in benzene-d_6, partial isomerization to [*SP*-4-4] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II), **(2')** was observed as shown in Scheme 10. In C_6D_6, efforts to quantify the ratio of products and determine whether the two species are truly in equilibrium have been hampered by the formation of significant amounts of platinum black. This may imply that under these conditions **2'** may decompose on a time scale relatively similar to that of isomerization.

[39] Pregosin, P. S.; Kurz, R. W. NMR 16: Basic Principles and Progress, Grundlagen und Fortschrife; Diehl, P.; Fluck, E., eds.; Springer-Verlag: New York, NY, 1979.



Scheme 10. Partial isomerization of N[CN]Pt(CO)(Me) (2) to N[CN]Pt(Me)(CO) (2')

A similar isomerization was not observed on heating **2** in THF-d_8 at 68°C for comparable lengths of time. In the presence of even small amounts of CO in THF-d_8, the isomerization between **2** and **2'** was found to be significant although not complete even after several days of heating at 68 °C. This result implies that in THF-d_8 the isomerization may be catalyzed by CO and proceed through a 5-coordinate intermediate, **A**, as shown in Scheme 11.



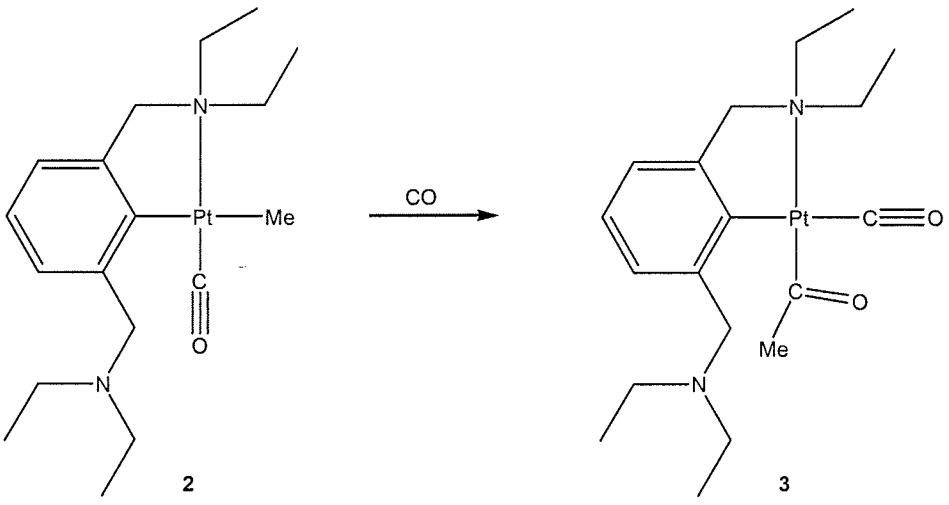
Scheme 11. Isomerization between N[CN]Pt(CO)(Me) (2) and N[CN]Pt(Me)(CO) (2') through intermediate A

Intermediate **A** is most likely capable of isomerization through a series of square pyramidal and trigonal bipyramidal forms. The barriers to these isomerizations are not known but are presumably low, as evidenced by the isomerization of **2** and **2'**.

2' has only been partially characterized, as it has never been isolated. IR spectra of mixtures containing **2'** indicated a CO stretching frequency of 2041 cm^{-1}, consistent with CO bound to Pt. The other key piece of evidence in support of the proposed structure for **2'** is the ^{1}H NMR spectrum of mixtures thought to contain **2'**, in which the $^{2}J_{Pt\text{-}H}$ value for the Pt bound methyl group is 88 Hz. This value is more than double that of **2** (42 Hz), and is consistent with a methyl group trans to a weaker ligand such as an amine arm.[39]

Formation of an acyl complex in THF

In the presence of CO over several hours to days in THF, benzene-d_6, toluene-d_8, or dichloromethane-d_2, **2** generates [*SP*-4-3] ((κ-*N*,*C*-2,6-bis(diethylaminomethyl)-phenyl)acylcarbonyl platinum(II), **(3)** as shown in Scheme 12.

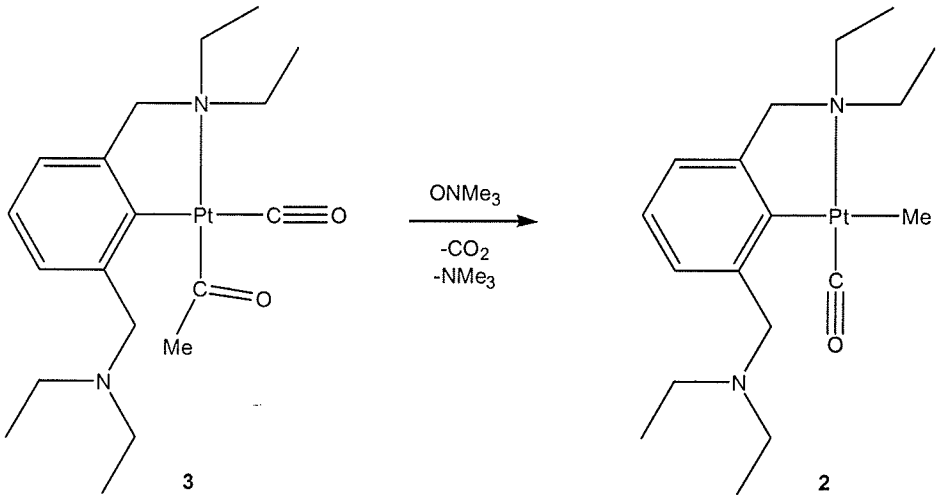


Scheme 12. Reaction of N[CN]Pt(CO)(Me) (2) with CO to form N[CN]Pt(Ac)(CO) (3)

The IR spectrum of **3** indicates CO stretching frequencies of 2063 cm^{-1} and 1656 cm^{-1}. The higher frequency is consistent with a Pt bound CO, while the lower frequency is consistent with a metal acyl.[40] This product was partially characterized by CHN combustion analysis, as well as ^{1}H NMR, ^{13}C NMR, HMQC and HMBC experiments in THF-d_8.[41] A sample of **3** has been generated on a preparatory scale and successfully recrystalized from a layered mixture of dichloromethane and pentane in 20% yield, and it may be possible to grow x-ray-quality crystals for absolute stereochemical characterization.

Decarbonylation of N[CN]Pt(Ac)(CO) (3) using Trimethylamine *N*-oxide

Trimethylamine *N*-oxide, a carbon monoxide abstraction agent, was allowed to react with **3** in THF-d_8, tolune-d_8, dioxane, and DCM-d_2 to remove an equivalent of CO as shown in Scheme 13.

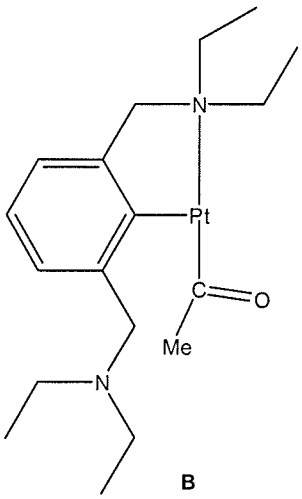


Scheme 13. Reaction of N[CN]Pt(Ac)(CO) (3) with trimethylamine N-oxide to form N[CN]Pt(CO)(Me) (2)

[40] Rulke, R. E.; Kaasjager, V. E.; Kliphius, D.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1996**, *15*, 668.

[41] The characterization of **3** thus far is incomplete and does not rule out all other structures. Repeating 2D and ^{13}C NMR experiments at higher sample concentrations and in different solvents will allow for more thorough characterization.

At room temperature, 68 °C and at 100 °C, this reaction afforded exclusively **2** and no appreciable amount of **2'** regardless of the solvent used. Exploring this reaction at a variety of temperatures excludes the possibility that at higher temperatures, similar to those discussed in future experiments, this reaction loses its selectivity. Likewise, obtaining similar results in a variety of both coordinating and non-coordinating solvents suggests that the solvent is not involved mechanistically. The presumed intermediate in this CO abstraction is the three-coordinate species, **B**, shown in Figure 4.



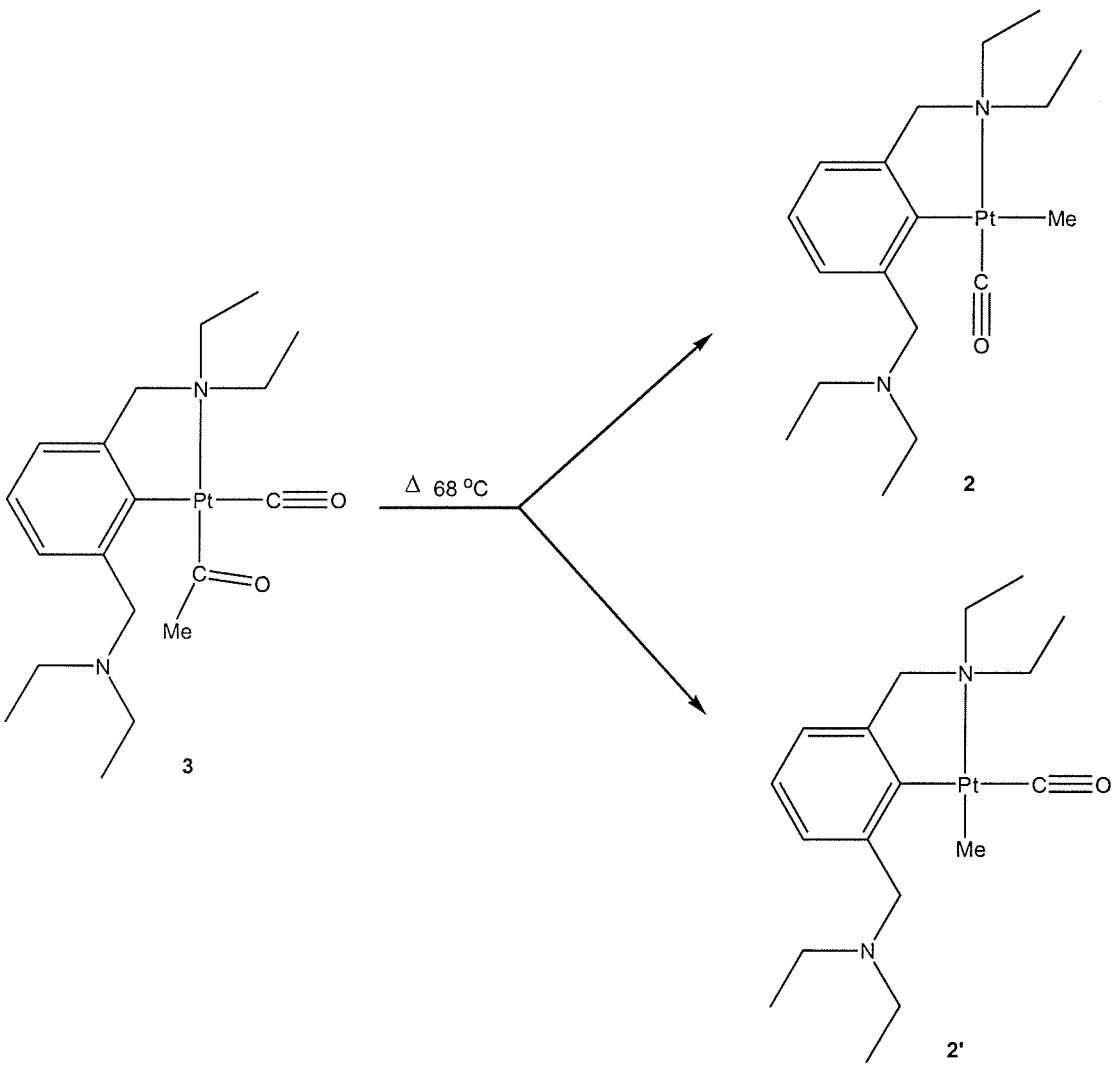
B

Figure 4. Three-coordinate intermediate, B

Intermediate **B** presumably then undergoes a methyl migration to form **2**. As **2'** is not observed, isomerization of **B** is not kinetically accessible under these reaction conditions.

Thermolysis of N[CN]Pt(Ac)(CO) (3)

Another method of removing CO from **3** is by thermolysis. **3** was heated in THF-d_8 to generate a mixture of **2** and **2'** as shown in Scheme 14.



Scheme 14. Heating N[CN]Pt(Ac)(CO) (3) to generate N[CN]Pt(CO)(Me) (2) and N[CN]Pt(Me)(CO) (2')

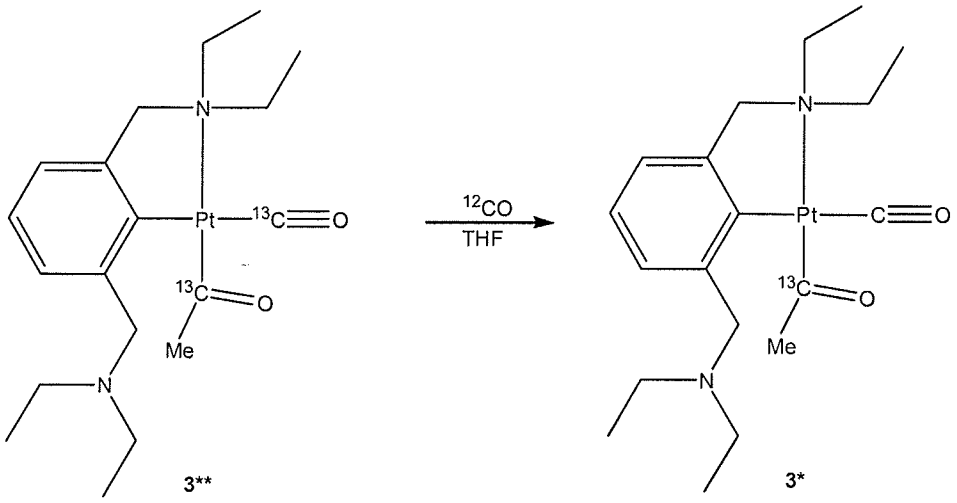
When the reaction was performed at 68 °C in a J-Young tube, **2** and **2'** appeared to form at relatively similar rates.

Because CO is known to promote isomerization between **2** and **2'**, the reaction was repeated with vigorous stirring under a continuous flow of argon to minimize the amount of CO in the system. A mixture of **2** and **2'** was still observed however **2** was formed faster at early reaction times.

The thermolysis of **3** was also carried out at in THF-d_8 in a flame sealed NMR tube at 100 °C. In this experiment the reaction mixture appeared to approach equilibrium after 1 day in which the ratio of **2'** to **2** was approximately 2:1. Allowing this mixture to sit at room temperature for three weeks resulted in a reaction mixture containing **2'** and **3** but no **2**. These results suggest that **2'** is slightly favored thermodynamically but its formation is significantly favored kinetically.

Labeling Results

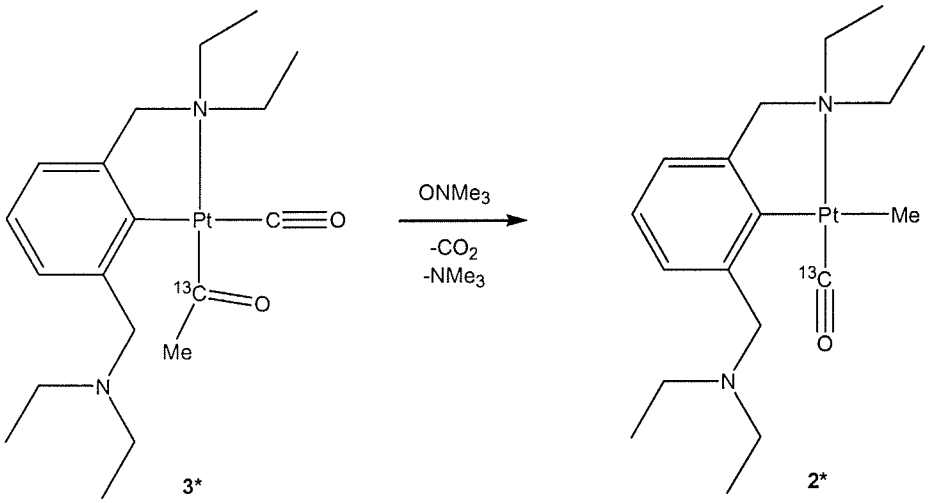
Placing **2** in a solution of bendene-d_6 or THF-d_8 under an atmosphere of ^{13}CO results in essentially quantitative exchange of ^{13}CO for ^{12}CO within minutes resulting in the formation of **2*** (* indicating a ^{13}C label). Placing **3**** (doubly ^{13}C labeled **3** synthesized using ^{13}CO) under an atmosphere of ^{12}CO in THF solution results in nearly quantitative exchange of the linear ^{13}CO for ^{12}CO over several days. The product of this reaction is **3*** in which the CO integrated into the acyl structure is labeled while the linear CO is not as shown in Scheme 15.



Scheme 15. Generation of N[CN]Pt(Ac)*(CO) (3*)

This reaction could conveniently be monitored using IR spectroscopy as the linear ^{13}CO stretch is at 2017 cm^{-1} vs. 2064 cm^{-1} for the linear ^{12}CO.

The decarbonylation of **3** using trimethylamine *N*-oxide was then repeated using **3***. The experiment resulted in almost exclusive formation of **2*** as shown in Scheme 16 with the small amount of **2** observed being attributed to a small amount of **3** as an impurity in the starting **3***.



Scheme 16. Reaction of N[CN]Pt(Ac)*(CO) (3*) with trimethylamine *N*-oxide

The final reaction mixture was characterized by IR spectroscopy and showed a strong peak at 2006 cm^{-1} consistent with **2***.This selectivity shows conclusively that the CO abstracted by the trimethylamine *N*-oxide is abstracted from **3** rather than a species analogous to intermediate **A** in which both the labeled and unlabeled CO fragments are linear and equally likely to be abstracted.

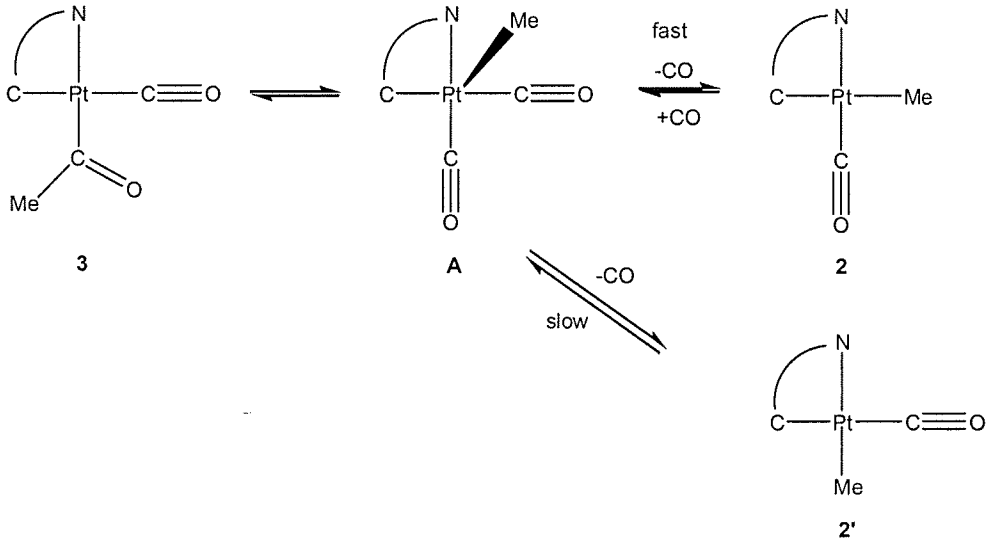
Thermolysis experiments were also carried out using **3***. Given that **2** is known to exchange CO rapidly, it is unsurprising that under sealed conditions, scrambling of the label to form **2**, **2***, **2'**, and **2'*** was observed. Scrambling was also observed when the reaction was run under a flow of argon. Because of significant overlap of the IR peaks

for the various compounds it could not be determined whether scrambling occurred within **3*** prior to its conversion to **2** and **2'** or whether the extent of scrambling was constant throughout the reaction. Eventually this reaction will be performed on a larger scale such that aliquots containing enough material to monitor the scrambling by ^{13}C NMR peak heights can be removed.

Two Mechanistic Proposals

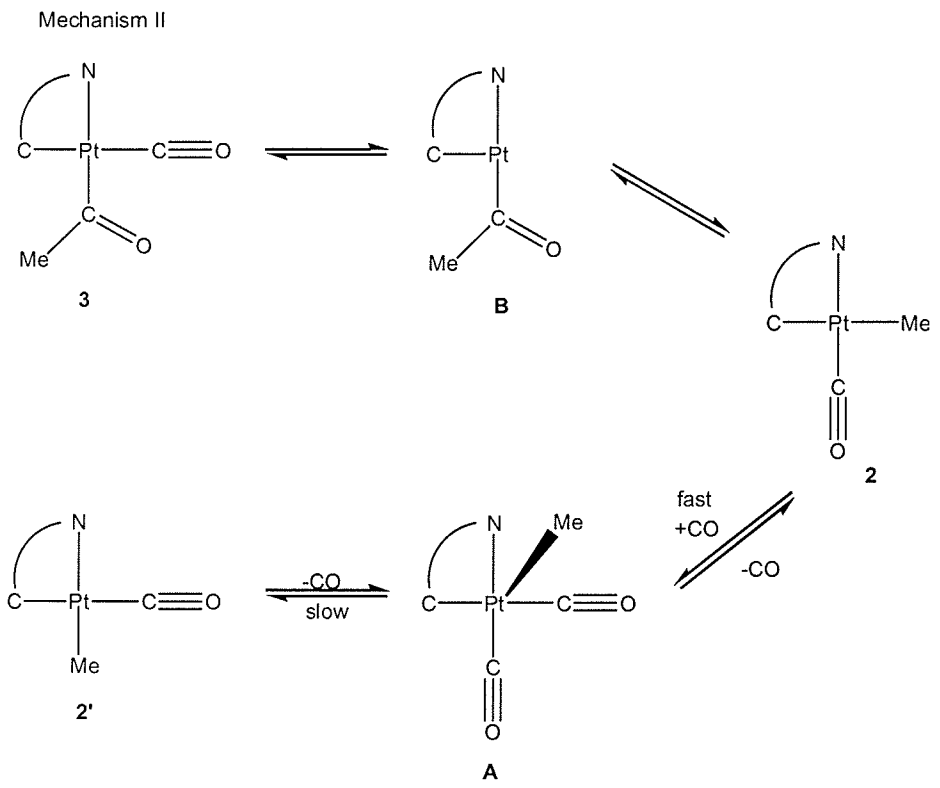
Based on the data gathered, two mechanisms for the decarbonylation of **3** seem plausible. The first possibility (Mechanism I, Scheme 17) involves initial methyl group migration into an axial position to form **A**. Given the fact that CO promotes isomerization between **2** and **2'** (Scheme 11) on the timescale of the reaction at the same temperature, **A** must be kinetically accessible and must be able to form both **2** and **2'**.

Mechanism I



Scheme 17. Mechanism I

Alternatively, **3** could undergo a loss of CO to form **B**, the proposed intermediate in the reactions with trimethylamine *N*-oxide as shown in Mechanism II, Scheme 18.



Scheme 18. Mechanism II

In this mechanism, intermediate **B** then undergoes a methyl migration to form **2**. In this mechanism, **2'** is formed exclusively from **2**, proceeding via coordination of CO to form **A** which can then undergo isomerization and CO release to afford **2'**.

At this time the two possibilities can not be distinguished. Furthermore, experiments performed thus far can not thoroughly eliminate other mechanistic possibilities such as the involvement of the uncoordinated amine arm of the ligand, though it is not clear what role this potential ligand might play. Mechanisms involving solvent are disfavored because thermolysis experiments have yielded similar results in both coordinating and non-coordinating solvents and in both polar and non-polar solvents.

It is hoped that further work will be able to distinguish between Mechanisms I and II in the thermolysis reaction and its microscopic reverse, carbonyl insertion. The rate laws for these proposed mechanisms will be difficult to distinguish experimentally. It is hoped that Eyring analysis will lead to an entropy of activation value unambiguously indicative of either an associative or dissociative mechanism.

Conclusion

Three new Pt-CO compounds, **2**, **2'**, and **3** were generated and characterized by ^{1}H NMR (**2**, **2'**, and **3**), ^{13}C NMR (**2** and **3**), and C,H,N analysis (**3**). In THF, **2** and **2'** were found to isomerize in the presence of CO but not appreciably in the absence thereof, implicating a five coordinate intermediate, **A**, in the isomerization mechanism. The reaction of **3** with trimethylamine *N*-oxide results exclusively in the formation of **2**, a reaction believed to proceed through intermediate **B**. Two mechanisms for the formation of **2** and **2'** from the thermolysis of **3**, one (Mechanism I) in which **A** is a common intermediate in the formation of both **2** and **2'**, and the other (Mechanism II) in which **B** is considered to be the intermediate in the conversion of **3** to **2**, and **A** is the intermediate in the interconversions between **2** and **2'**.

Experimental

General Procedures

All manipulations, with the exception of the preparation of samples for IR spectroscopy, were performed under a nitrogen atmosphere in a VAC Atmospheres glovebox or on a Schlenk/vacuum line using standard techniques. All glassware was oven dried prior to use. Proteo-solvents were dried by a Glass Contour solvent drying system. Deuterated solvents and ^{13}CO were purchased from Cambridge Isotopes and used as received. CO was purchased from Airgas and used as received without further purification or drying. **1** was synthesized according to a published procedure.[31] All other chemicals were purchased from Aldrich and used as received. IR spectra were recorded on an AVATAR 370 FTIR in a CCl_4 solution cell using KBr plates. NMR spectra were recorded at 300 MHz on a Bruker AC300 spectrometer with a TecMag console upgrade or at 400 MHz on a Bruker DPX 400 spectrometer. Combustion analysis was carried out by Atlantic Microlabs, Norcross, GA.

Preparation of [SP-4-3] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)acylcarbonyl platinum(II), (3)

In a resealable ampoule, **1** (250 mg, 0.546 mmol) was dissolved in 12 mL THF. The sample was frozen and the headspace evacuated. The ampoule was then held at -78 °C for 5 min. while ~1 atm CO was added (~2 mmol). The reaction was warmed to room temperature and left isolated from light for 4 days. The solution was then filtered through glass wool/ Celite and the solvent removed *in vacuo* to yield solid **3** (206 mg, 0.401 mmol, 73%). The product was recrystalized from layered dichloromethane and pentane (56 mg, 0.11 mmol, 20%). ^1H NMR data are reported in Table 1 using the labeling

system shown in Figure 5.[42] ^{13}C NMR (THF-d_8, 100.6 MHz) δ = 11.28 ($^3J_{Pt-C}$ = 15 Hz), 12.60, 47.50, 52.78, ($^3J_{Pt-C}$ = 72 Hz), 67.14, 122.25 ($^3J_{Pt-C}$ = 30 Hz), 126.74, 127.44 ($^3J_{Pt-C}$ = 59 Hz), 149.98, 152.07, 161.44, 166.89, 182.42, 206.90. IR: ν_{CO} = 2063 cm^{-1} (C≡O), 1656 cm^{-1} (C=O). C,H,N combustion analysis: Calc'd C 44.44 %, H 5.89%, N 5.45%; Found C 44.32 %, H 5.79%, N 5.43%.

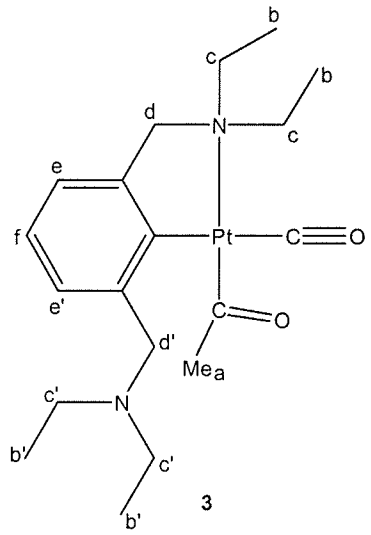


Figure 5. N[CN]Pt(Ac)(CO) (3) labeled for ^1H NMR assignment

[42] Data are reported in a variety of solvents as future work may explore this system in a variety of solvents.

Table 1. ^{1}H NMR data for N[CN]Pt(Ac)(CO) (3)

proton	benzene-d_6 δ		$^3J_{H-H}$	$^3J_{Pt-H}$	toluene-d_8 δ		$^3J_{H-H}$	$^3J_{Pt-H}$	THF-d_8 δ		$^3J_{H-H}$	$^3J_{Pt-H}$
a	2.56	s	-	†	2.5	s	-	7	2.27	s	-	18
b#	0.63	t	6	-	0.71	t	7	-	0.96	t	7	-
b'#	1.08	t	7	-	1.07	t	7	-	1.28	t	7	-
c*	2.2	m	-	-	2.26	m	-	-	2.44	q	7	-
	2.46	m	-	-	†	-	-	-	-	-	-	-
c'	2.62	q	7	-	2.59	q	7	-	3.07	q	7	-
d#	3.45	s	-	-	3.46	s	-	-	3.49	s	-	-
d'#	3.95	s	-	-	3.84	s	-	-	4.1	s	-	-
e#	6.93	d	6	-	6.89	d	7	-	7.34	d	7	-
e'#	7.9	d	7	-	7.78	d	8	-	6.97	m	-	-
f	7.22	t	7	-	7.15	t	8	-	6.97	m	-	-

proton	MeCN-d_3 δ		$^3J_{H-H}$	$^3J_{Pt-H}$	DCM-d_2 δ		$^3J_{H-H}$	$^3J_{Pt-H}$	nitrobenzene-d_5 δ		$^3J_{H-H}$	$^3J_{Pt-H}$
a	2.33	s	-	10	2.4	s	-	-	2.57	s	-	†
b#	0.94	t	7	-	0.97	t	7	-	1	t	7	-
b'#	1.25	t	7	-	1.28	t	7	-	1.24	t	7	-
c*	3.04	m	-	-	3.05	m	(3)	-	3.012	m	(3)	-
	-	-	-	-	-	-	-	-	-	-	-	-
c'	2.41	q	7	-	2.44	q	7	-	2.51	q	7	-
d#	3.39	s	-	-	3.41	s	-	-	3.72	s	-	-
d'#	4.08	s	-	-	4.07	s	-	-	4.06	s	-	-
e#	6.76	bm	-	-	7.02	bm	-	-	7.15	bm	-	-
e'#	6.76	bm	-	-	7.33	d	6	-	7.54	d	7	-
f	7.27	t	5	-	7.02	bm	-	-	7.15	bm	-	-

The assignments distinguishing b and b', d and d', and e and e' could not be determined in solvents where HMQC and HMBC experiments have not been performed.
*Two chemical shifts are reported for solvents in which the protons appear distinctly diastereotopic
†Unresolved

Preparation of [SP-4-2] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II),(2)

In a typical experiment, a J. Young NMR tube was charged with **1** (10 mg, 0.0219 mmol) and 0.5 mL deuterated solvent. The sample was frozen and the headspace evacuated. The sample was then cooled to -78 °C and ~1 atm CO (0.2 mmol) was added over 1 min. The reaction was warmed and shaken resulting in **2**. ^{1}H NMR data reported in

Table 2 with the protons identified in Figure 6. ^{13}C NMR (THF-d_8, 100.6 MHz) δ =1.62 ($^1J_{Pt-C}$ = 374 Hz), 11.67 ($^3J_{Pt-C}$ = 24 Hz), 12.10, 46.63, 53.82, 65.27 ($^3J_{Pt-C}$ = 45 Hz), 70.86 ($^3J_{Pt-C}$ = 14 Hz), 120.88 ($^3J_{Pt-C}$ = 16.46), 125.08, 126.90 ($^3J_{Pt-C}$ = 27), 145.80 ($^2J_{Pt-C}$ = 50 Hz), 147.98, 172.39 ($^1J_{Pt-C}$ = 1930 Hz), 173.37 ($^1J_{Pt-C}$ = 662 Hz). IR: ν_{CO} = 2055 cm^{-1}.

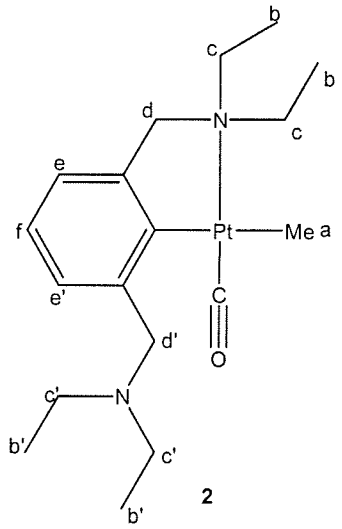


Figure 6. N[CN]Pt(CO)(Me) (2) labeled for ^1H NMR assignment

Table 2. NMR data for N[CN]Pt(CO)(Me) (2) in various solvents.

proton	benzene-d_6				toluene-d_8				THF-d_8			
	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$
a	0.68	s	-	42	0.6	s	-	48	0.35	s	-	43
b#	1.03	t	7	-	0.84	t	6	-	0.99	t	7	-
b'#	0.81	t	6	-	1.04	t	7	-	1.27	t	7	-
c*	2.33	m	-	-	2.36	m	-	-	3	m	-	-
	2.48	m	-	-	2.5	m	-	-	3.14	m	-	-
c'	2.65	q	7	-	2.63	q	7	-	2.54	q	7	-
d#	3.51	s	-	29	3.51	s	s	28	3.6	s	-	-
d'#	3.92	s	-	-	3.84	s	-	-	4.14	s	-	29
e#	7.12	d	7	-	7.61	d	7	-	7.09	d	7	-
e'#	7.71	d	7	-	7.07	d	7	-	7.21	d	7	-
f	7.29	t	7	-	7.22	t	7	-	6.95	t	7	-

proton	MeCN-d_3				DCM-d_2				nitrobenzene-d_5			
	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$
a	0.32	s	-	35	0.36	s	-	43	0.43	s	-	42
b#	0.96	t	n/a	-	1	t	n/a	-	0.97	t	7	-
b'#	1.22	t	n/a	-	1.27	t	n/a	-	1.2	t	6	-
c*	2.78	m	-	-	2.95	m	-	-	2.88	m	-	-
	†	-	-	-	3.12	m	-	-	3.04	m	-	-
c'	2.51	q	7	-	2.55	q	6	-	2.56	q	7	-
d#	3.57	s	-	-	3.6	s	-	-	3.67	s	-	-
d'#	4.14	s	-	-	4.12	s	-	28	4.08	s	-	28
e#	6.71	d	6	-	7.16	d	5	-	7.26	d	7	-
e'#	6.85	d	n/a	-	7.23	d	n/a	-	7.38	d	7	-
f	7.16	t	7	-	7.04	t	7	-	7.18	t	7	-

The assignments distinguishing b and b', d and d', and e and e' could not be determined in solvents where HMQC and HMBC experiments have not been performed.
*Two chemical shifts are reported because the protons are diastereotopic
†Unresolved

Thermolysis of N[CN]Pt(Ac)(CO) (3)

In a typical experiment, a J. Young NMR tube was charged with **3** (10 mg, 0.022 mmol), which was then dissolved in 0.5 mL deuterated solvent. The sample was placed in a 68 °C bath and isolated from light. A mixture of **2** and [*SP*-4-4] ((κ-*N,C*-2,6-bis(diethylaminomethyl)-phenyl)carbonylmethyl platinum(II) **(2')** formed within hours. This reaction has also been performed in flame sealed NMR tubes heated to 100 °C. Though not isolated, **2'** was characterized as follows: ^{1}H NMR data are reported in Table 3 with the labels defined in Figure 7. IR: ν_{CO} = 2041 cm^{-1}.

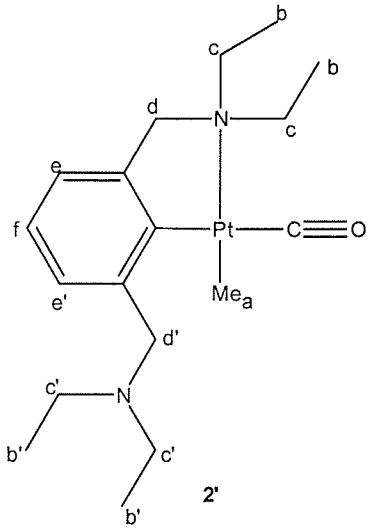


Figure 7. N[CN]Pt(Me)(CO) (2') labeled for ^{1}H NMR assignment

Table 3. ^{1}H NMR data for N[CN]Pt(Me)(CO) (2')

	benzene-d_6				toluene-d_8				THF-d_8			
proton	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$
a	1.65	s	-	92	1.56	s	-	94	1.06	s	-	89
b$^{\#}$	0.72	t	8	-	†	-	-	-	0.97	t	, 7	-
b'$^{\#}$	0.95	t	7	-	†	-	-	-	1.27	t	n/a	-
c*	†	-	-	-	†	-	-	-	3.17	m	-	-
	†	-	-	-	†	-	-	-	3.06	m	-	-
c'	2.43	q	7	-	†	-	-	-	2.42	q	7	-
d$^{\#}$	3.6	s	-	~18	3.52	s	-	-	3.75	s	-	-
d'$^{\#}$	4.13	s	-	-	4.06	s	-	-	4.14	s	-	-
e$^{\#}$	7.71	d	6	-	7.6	d	7	-	7.36	d	7	-
e'$^{\#}$	7.1	d	n/a	-	†	-	-	-	6.9	bm	-	-
f	7.3	t	7	-	7.22	t	8	-	6.9	bm	-	-

	MeCN-d_3				DCM-d_2				nitrobenzene-d_5			
proton	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$	δ		$^3J_{H-H}$	$^2J_{Pt-H}$
a	~0.98	s	-	~90								
b$^{\#}$	†	-	-	-								
b'$^{\#}$	†	-	-	-								
c*	~3.14	q	n/a	-								
	-	-	-	-								
c'	†	-	-	-								
d$^{\#}$	3.69	s	-	-								
d'$^{\#}$	†	-	-	-								
e$^{\#}$	†	-	-	-								
e'$^{\#}$	†	-	-	-								
f	†	-	-	-								

$^{\#}$ The assignments distinguishing b and b', d and d', and e and e' could not be determined in solvents where HMQC and HMBC experiments have not been performed.
*Two chemical shifts are reported when the protons are distinctly diastereotopic
†Unresolved

Thermolysis of N[CN]Pt(Ac)(CO) (3) under continuous argon flow

In a typical experiment, **3** (30 mg, 0.058 mmol) was dissolved in 5 mL THF in a 15 mL round bottom flask fitted with a condenser covered by a septum. Argon was bubbled into the solution directly and the apparatus was equipped with a vent needle attached to a mineral oil bubbler. Solutions were stirred vigorously and heated to reflux with additional solvent added every two hours to maintain volume. Aliquots of the reaction mixture were removed at regular intervals and analyzed by ^{1}H NMR and IR spectroscopy.

Reaction of N[CN]Pt(Ac)(CO) (3) with trimethylamine *N*-oxide

In a J. Young NMR tube, **3** (10 mg, 0.020 mmol) and trimethylamine *N*-oxide (1.46 mg, 0.0195 mmol) were dissolved in 0.5 mL deuterated solvent. **2** and trimethylamine were observed as products within minutes. For reactions carried out at elevated temperatures, trimethylamine *N*-oxide was dissolved in deuterated solvent in a screw-cap NMR tube and heated to the desired temperature. A solution of **3** was prepared in 200 μL of deuterated solvent and added by syringe.

Synthesis of N[CN]Pt(Ac)*(CO) (3*)

In a typical experiment, **3**** (100 mg, 0.19 mmol) was dissolved in 5 mL THF and placed in a 25 mL resealable ampoule equipped with a stirbar. The sample was frozen and the headspace evacuated. The ampoule was then charged with ~1 atm CO at room temperature for one minute. The reaction was stirred and after one day the sample was degassed and charged with fresh CO (~1 atm). The reaction mixture was then stirred for another day and degassed. The material was used without further purification. The progress of the label incorporation was followed by IR spectroscopy throughout.

Formation of N[CN]Pt(CO)*(Me) (2*)

In a typical experiment, a sample of **2** (10mg, 0.021mmol) was dissolved in 0.5 mL of THF-d_8 or C_6D_6 in a J. Young NMR tube. The sample was frozen and the headspace evacuated. The sample was then charged with 1.1 atm ^{13}CO at room temperature for 1 minute. The mixture was shaken and a ^{13}C NMR spectrum recorded. No further change was observed hours later.

Acknowledgements

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